UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

March 2, 2011

MEMORANDUM

SUBJECT: Review of Leach Rate Data for Shelter Island Plus Deep Blue Color Antifouling Paint containing and Zinc Pyrithione (4.15%) and Tralopyril (5.92 %) , EPA File Symbols 74681-E1

PC Code(s): 088002, 119093	DP Barcode(s)/No(s): D385363
Decision No.: 442348	Registration No(s).: 74681-E1
Petition No(s).: NA	Regulatory Action: New Registration (Section 3)
Risk Assess Type: Multiple Chemicals	Case No(s).: NA
TXR No.: NA	CAS No(s): 13463-41-7; Zinc Pyrithione 122454-29-9; Tralopyril
MRID No(s).: 48297806	40 CFR: NA

FROM: James Breithaupt, Agronomist
Risk Assessment and Science Support Branch (RASSB)
Antimicrobials Division (7510P)

TO: Marshall Swindell, Leader, Team 33
Abigail Downs, Risk Manager Reviewer
Regulatory Management Branch I
Antimicrobials Division (7510P)

THRU: Siroos Mostaghimi, Peer Review
Risk Assessment and Science Support Branch (RASSB)
Antimicrobials Division (7510P)

Nader Elkassabany, Chief
Risk Assessment and Science Support Branch (RASSB)
Antimicrobials Division (7510P)

Chemical Name: Zinc Pyrithione

Chemical Name: Tralopyril (Econea)

INTRODUCTION: [redacted] has submitted the Special Leaching Study for Antifouling Paint Deep Blue Code Lag 2008-036 containing 4.15 % zinc pyrithione (PC Code 088002) and 5.92 % tralopyril (ECONEA, PC Code 119093). The registrant used the ASTM Standard Test Methods D6903-07 that is acceptable by the Agency to fulfill the Special Leaching Study Data Requirements for Antifouling Paints.

BACKGROUND:

Zinc pyrithione (PC Code 088002) and Tralopyril (PC Code 119093) are active ingredients in Shelter Island Plus Deep Blue Paint, File Symbol 74681-El. The submitted study was conducted to determine the leaching rates of zinc pyrithione and tralopyril

CITATION:

Determination of the Leach Rate of Zinc Pyrithione and Tralopyril (Code Number 74681-El)) Deep Blue in Synthetic Seawater by Amanda Tunink, ABC Laboratories, Inc., 7200 E. ABC Lanek Columbia, Mo 65202 (MRID No. 48297806).

DATA EVALUATION: Attached.

CONCLUSIONS:

The test materials employed in the test were zinc pyrithione (PC Code: 88002; CAS Number: 13463-41-7) and tralopyril (PC Code 119093, CAS Number 122454-29-9).

Table 1. Leaching Rates for Zinc Pyrithione and Tralopyril

	Zinc Pyrithione			Tralopyril		
Leaching rates	5 oC	15 oC	25 oC	5 oC	15 oC	25 oC
Maximum (ug/cm2/day)	6.3	11.7	14.3	2.2	5.3	17.7
Minimum (ug/cm2/day)	3.5	4.1	4.7	0.4	1.7	4.7
Average (ug/cm2/day)	4.2	5.3	8.5	1.3	3.4	11.6
Cumulative (14-days, ug/cm2)	71	83	150	14	41	120
Cumulative (45-days, ug/cm2)	189	237	384	59	155	522

RECOMMENDATIONS:

The submitted Special Leaching Study is acceptable and reflects the guideline specified for the ASTM Standard Test Method, D6903-07 for aqueous availability. Risk Assessment and Science Support Branch recommends that the Special Leaching Study for the zinc pyrithione (PC Code: 088002 and tralopyril (PC Code 119093) be accepted in support of Shelter Island Plus Deep Blue Antifoulant Paint (EPA File Symbol 74681-El)) End-Use Product registration.

Determination of the Leach Rate of Organic Biocides at Three Different Temperatures from the Antifoulant Paint Code No. Lag 2008-036-Blue, in Substitute Ocean Water

DATA EVALUATION REPORT

PRODUCT FORMULATION: Shelter Island Plus Deep Blue Antifoulant Paint.

ACTIVE INGREDIENTS: (Zinc Pyrithione) Bis(1-hydroxy-2(1H)-pyridinethionato-O-S) Zinc (4 %) and Tralopyril (3-bromo-5-(4-chlorophenyl)-4-cyano-1H-pyrrole-2-carboxylic acid), 5.9 %

BACKGROUND:

The submitted leaching study was conducted to determine the leach rate of Zinc Pyrithione and Tralopyril from Antifouling Paint Code No. Lag 2008-036

CITATION:

Title:	Determination of the Leach Rate of Organic Biocides at Three Different Temperatures from the Antifouling Paint Code No. Lag 2008-036-Blue, in Substitute Ocean Water.
Study Author:	Amanda Tunink.
Date:	November 12, 2009.
Performing Laboratory:	ABC Laboratories, Inc., 7200 E. ABC Lane, Columbia, Mo 65202
Sponsor:	[redacted]
Study ID.:	65299
MRID No.:	48297806.

GUIDELINE No.: ASTM Designation: D6903-07.

EXECUTIVE SUMMARY:

The study was conducted to determine the leach rate of Zinc Pyrithione® from Shelter Island Deep Blue Antifouling Paint into substitute seawater under laboratory conditions over a period of 45 days. The study was conducted according to ASTM Designation: D6903-07 and in compliance with USEPA 40 CFR Part 160.

A *ca.* 10 cm band of formulated test paint, with an area of *ca.* 200 cm^2, was applied to polycarbonate cylinders (*ca.* 6.3 cm i.d., *ca.* 17.5 cm length). A total of three coats of paint were applied to each cylinder. The cylinders were then suspended in a rectangular glass holding tank containing substitute seawater maintained at 22.9-25.0°C with pH ranging from 7.9-8.1 and salinity ranging from 33-34 ppt. Each cylinder was positioned so that the painted surfaces were completely immersed in the water. The seawater was continuously circulated through cartridges containing carbon and ion-exchange resin at a rate of 2 to 8 changes per hour. Measurements of water temperature, pH, and salinity were conducted throughout the study.

Dynamic leach rates were determined by rotating the three painted cylinders and one unpainted blank cylinder in synthetic seawater. After 60 minutes of rotation at *ca.* 60 rpm, the cylinders were returned to the holding tank and samples of the seawater were transferred to amber bottles for analysis. Leach rate measurements were taken at Days 1 (*ca.* 24 hours following immersion of the cylinders in the holding tank) 3, 7, 10, 14, 21, 23, 28, 30, 35, 38, 42, and 45. Samples of the holding tank water and the reservoir tank water were also collected at these sampling intervals.

The temperature in the holding tank ranged from 22.9-25.0°C throughout the study. The pH of the seawater ranged from 7.9-8.1 and the salinity ranged from 33-34 ppt.

The synthetic seawater was analyzed for zinc pyridine and tralopyril using HPLC-UV detection. The seawater samples and analytical standard solutions were first treated with EDTA and pyridine disulfide (PDS). The samples were allowed to stand for 30 minutes prior to HPLC analysis. Zinc pyrithione and tralopyril were identified by comparison to chromatograms of a derivatized reference standard.

The cumulative release rate of Zinc *Pyrithione®* was calculated by multiplying the average dynamic leach rates at each time point by the number of days in the interval represented by the time point and then summing the values. Peak, minimum, and average leaching rates for zinc pyrithione ranged from 6.3-14.3, 3.5-14.7, and 4.2-8.5 ug/cm^2/day, respectively. Cumulative leaching rates for 0-14 and 0-45 days ranged from 71-150 and 189-384 ug/cm2, respectively. Peak, minimum, and average leaching rates for tralopyril ranged from 2.2-17.7, 0.4-4.7, and 1.3-11.6 ug/cm^2/day, respectively. Cumulative leaching rates for 0-14 and 0-45 days ranged from 14-120 and 59-522 ug/cm2, respectively. These rates may be seen in Tables 1 above and 2 below.

The thickness of the paint on the cylinders was determined from the mean painted cylinder diameter and the mean unpainted cylinder diameter. The initial thickness of the paint layer on each cylinder ranged from 189-284 μm. Following the 45-day leaching, the thickness ranged from 66-134 μm. However, the weight or density of paint was not reported.

The content of zinc pyrithione and tralopyril in the holding tank, reservoir, and cylinder blank samples was <LOQ (0.26 μg/L) for all sampling intervals.

This study is scientifically sound and classified as acceptable. No significant deviations from good scientific practices were noted. It was not reported whether labware was treated prior to use in the study or whether the exposure surfaces of the test cylinders were prepared, i.e. sanded, prior to application of the test paint.

RESULTS SYNOPSIS:

Table 2. Leaching Rates for Zinc Pyrithione and Tralopyril

	Zinc Pyrithione			Tralopyril		
Leaching rates	5 oC	15 oC	25 oC	5 oC	15 oC	25 oC
Maximum (ug/cm2/day)	6.3	11.7	14.3	2.2	5.3	17.7
Minimum (ug/cm2/day)	3.5	4.1	4.7	0.4	1.7	4.7
Average (ug/cm2/day)	4.2	5.3	8.5	1.3	3.4	11.6
Cumulative (14-days, ug/cm2)	71	83	150	14	41	120
Cumulative (45-days, ug/cm2)	189	237	384	59	155	522

I. MATERIALS AND METHODS

Guideline followed: The study was modeled after ASTM Designation: D6903-07, "Test Method for Determination of Organic Biocide Release Rate from Antifouling Coatings in Substitute Ocean Water."

Compliance: The study was conducted in compliance with USEPA 40 CFR Part 160 (pp. 3-4). Signed and dated Data Confidentiality, GLP, Quality Assurance, and Certificate of Authenticity statements were provided (p. 4).

A. Materials:

1. Test Material: Shelter Island Plus, **Deep Blue, Code Lag 2008**-036 Supplied by [redacted]

Chemical Structure: See DER Attachment 1.

Description: **Blue liquid** .

Purity: **4.15 % Zinc pyrithione and 5.92 % tralopyril**

2. Synthetic Sea Water Solution:

Substitute seawater was prepared in two batches but no further information was provided. The salinity was adjusted to 33-34 parts per thousand using deionized water. The pH was adjusted to 7.9-8.1 using 0.1N NaOH (Fisher Lot # 026469/24).

B. Experimental Conditions:

1. Preliminary Study:

Preliminary experiments were not conducted.

2. Experimental Conditions:

Polycarbonate cylinders (*ca.* 6.34 cm i.d., *ca.* 17.5 cm length; 3 test cylinders, one control cylinder) fitted with 3 baffles were used (pp. 11-12). Foam brushes were used to apply a *ca.* 10 cm band of formulated test paint with an area of *ca.* 200 cm^2 to each cylinder. A total of three coats of paint were applied to each cylinder, allowing each coat to dry. The cylinders were placed under a fume hood shielded from light with opaque black plastic for *ca.* 20 hours, then transferred to an incubator maintained at 23.9-24.2°C for 7 days. The cylinders were then suspended in a rectangular glass holding tank containing *ca.* 35 L of substitute seawater maintained at 22.9-25.0°C with pH ranging from 7.9-8.1 and salinity ranging from 33-34 ppt. Each cylinder was positioned so that the painted surfaces were completely immersed in the water. A Phipps and Bird 6-paddle stirrer was used for rotating the test cylinders in the holding tanks. The substitute seawater was continuously circulated through cartridges containing carbon and ion-exchange resin at a rate of 2 to 8 changes per hour. The cylinders and the inlet and outlet to each carbon filter were positioned in the holding tank to give a slow and uniform flow of water.

For the determination of dynamic leach rate measurements, the cylinders were rotated at *ca.* 60 rpm in *ca.* 1.5 L of synthetic seawater (p. 12). After 60 minutes, the cylinders were returned to the holding tank and samples (20 mL) of the seawater were transferred to amber bottles (40 mL) containing pyridine disulfide (1.0 mL) for analysis, to which saturated EDTA reagent (1.0 mL) was added.

Leach rate measurements were taken at Days 1 (*ca.* 24 hours following immersion of the cylinders in the holding tank) 3, 7, 10, 14, 21, 23, 28, 30, 35, 38, 42, and 45. Samples of the holding tank water and the reservoir tank water were also collected at these sampling intervals.

For the holding tank, measurements of temperature, pH, and salinity were conducted daily (p. 12). For the artificial seawater reservoir, measurements of temperature, pH, and salinity were conducted at the start of the test and daily thereafter.

3. Supplementary Experiments:

Supplementary experiments were not conducted as a part of this study.

C. Analytical Methods:

The synthetic seawater was analyzed for zinc pyrithione and tralopyril using HPLC (pp. 12-13). However, zinc pyrithione cannot be measured directly by HPLC without prior derivatization.

Therefore, aliquots of the water samples and analytical standards were treated with EDTA and pyridine disulfide (PDS). The samples were allowed to stand for *ca.* 30 minutes prior to HPLC analysis under the following operating conditions: YMC ODS-AQ C18 S-5 120A column (4.6 mm x 250 mm; 5 µm particle size), mobile phase of acetonitrile:HPLC water (30:70, v:v), flow rate of 1.5-2.0 mL/minute, and UV detection (234 nm). Zinc pyrithione was identified by comparison to chromatograms of a derivatized reference standard of zinc pyrithione The Limits of Detection (LOD) for zinc pyrithione and tralopyril 2.2 ng/l and 2.4 and 2.2 ug/l, respectively.

The cumulative release rate of Zinc *Pyrithione®* was calculated by multiplying the average dynamic leach rates at each time point by the number of days in the interval represented by the time point, summing the values (p. 14), and dividing by the number of days elapsed.

To determine the paint thickness on the cylinders, the diameter of each cylinder was determined prior to paint application, at seven days after application, and at seven days after the end of the test (p. 15). The diameter measurements were performed in six locations on each cylinder. The thickness of the paint was determined as the difference of the mean painted cylinder diameter and the mean unpainted cylinder diameter, divided by 2.

II. RESULTS AND DISCUSSION

A. Test Conditions:

The study was conducted under laboratory conditions using synthetic seawater. The temperature in the holding tank ranged from 22.9-25.0°C throughout the study, the pH of the seawater ranged from 7.9-8.1, and the salinity ranged from 33-34 ppt.

B. Anomalies:

The study author did not report any problems encountered during the study period.

C. Summary:

Individual leach rates of Zinc *Pyrithione®* from the painted cylinders ranged from a high of 14.3 µg/cm^2/day at Day 1 to a low of 3.5 µg/cm^2/day at Day 38. A pseudo steady-state leach rate of 5.5 ± 0.9 µg/cm^2/day was obtained from Day 14 through Day 45. For zinc pyrithione, the pseudo steady leach rates (14-45 days) were 3.4, 4.4, and 6.7 ug/cm^2/day for 5, 15, and 25 °C, respectively. For tralopyril, the pseudo steady leach rates (14-45 days) were 1.3, 3.3, and 11.5 ug/cm^2/day for 5, 15, and 25 °C, respectively. Cumulative leaching rates of Zinc Pyrithione® from the paint were 71-150 and 189-384 µg/cm^2 through Day 14 and 189-384 µg/cm^2 through Day 45. Cumulative leaching rates of tralopyril from the paint were 71-150 ug/cm^2 through day 14 and 59-522 ug/cm^2 through day 45.

The initial thickness of the paint layer on each cylinder ranged from 220-230 µm. Following the 45-day leaching, the thickness ranged from 200-210 µm.

The content of Zinc *Pyrithione®* in the holding tank, reservoir, and cylinder blank samples was <LOQ (0.26 µg/L) for all sampling intervals.

III. STUDY DEFICIENCIES

None

IV. REVIEWERS COMMENTS

1. Prior to use, the Shelter Island Dark Blue Antifouling Paint and the reference standards reference substance were stored in the dark at room temperature (p. 10).

V. CONCLUSION

The study (MRID 48297806) satisfies the ASTM D6903-07 data requirement for Shelter Island Deep Blue Antifouling Paint.

VI. REFERENCES

1. ASTM. June, 2003. Test Method for Determination of Organic Biocide Release Rate From Antifouling Coatings in Substitute Ocean Water. D 6903-07. Annual Book of ASTM Standards.

Sign-off Date : 03/02/11
DP Barcode No. : D385363